Electron impact study of $C_6H_5^+$ fragment ion obtained from three molecules

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Abstract. $C_6H_5^+$ fragment ion produced from toluene, n-propylbenzene and acetophenone have been studied using an electron impact technique. The ionization efficiency data have been treated by the inverse convolution first differential technique. First and higher appearance energies for ions produced from the three precursors are reported. The heats of formation for the ions obtained at threshold from the three molecules are calculated.

Keywords. Electron impact study; differential technique; heat of formation; threshold; $C_6H_5^+$ fragment ion.

1. Introduction

Positive ion $C_6H_5^+$ ($m/z = 77$) is a significant contributor to the spectra of nearly all aromatic and related compounds. Although studies (Grubb and Meyerson 1963; Momigny *et al* 1962; Franklin and Carrol 1969) have been performed to establish its structure by determining heats of formation from different precursors, the structure and heat of formation of the ion are not well established. The conclusions regarding the structure of the ions appear to oscillate between phenyl ions having ΔH_f around $1170 \, \text{kJ mol}^{-1}$ and linear ions having ΔH_f around $1255 \, \text{kJ mol}^{-1}$. On the other hand Fisher *et al* (1964) succeeded in measuring ionization energy of the phenyl radical and calculated ΔH_f to be $1180 \, \text{kJ mol}^{-1}$. However, Momigny *et al* (1962) determined the heat of formation of $C_6H_5^+$ fragment ions from several linear C_6H_6 isomers and his data indicated that $C_6H_5^+$ fragment formed from linear compounds is always acyclic with $\Delta H_f = 1255 \, \text{kJ mol}^{-1}$. Franklin and Carrol (1969) had concluded that the previous measurements of the appearance energy (AE) of $C_6H_5^+$ ion from aromatic compounds could have involved excess energy which may or may not have resulted in ring opening.

The main purpose of the present study is the careful investigation of AE at threshold of $C_6H_5^+$ fragment ion produced from toluene, n-propylbenzene and acetophenone in order to determine ΔH_f values for the ions and to try to identify the ionic structures. The detection of the structure in the ionization efficiency (IE) curves of $C_6H_5^+$ ion obtained from the three molecules for 3–4 eV above threshold (obtained from the electron impact technique) is also of interest. By combining the inverse convolution procedure of Vogt and Pascual (1972) with the first derivative method we have been able to measure the appearance energy at threshold for $C_6H_5^+$ produced from the three

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molecules and determine the structure in ie curves. This combined technique was developed and examined previously by Selim (1982a) and applied by Selim and Helal (1982) for studying molecular ions of toluene, ethylbenzene and n-propylbenzene and to study $C_7H_7^+$ fragment ion obtained from these molecules.

2. Experimental technique

Ionization efficiency data are obtained using an Atlas CH-4 mass spectrometer with a normal electron impact ion source (AN4). The conditions of measurements and the method of calibration of the energy scale are the same as previously reported (Selim 1976). A sensitive electron multiplier is used for detecting the positive ions. The directly measured ie curves are smoothed by a 5-point smoothing technique (Savitzky and Golay 1964). The smoothed data are treated to obtain the first derivative (Savitzky and Golay 1964) ie curves, and then the inverse convolution procedure of Vogt and Pascual (1972) is applied to obtain the deconvoluted first differential ie curves. The complete details of the application of the combined technique have been reported elsewhere (Selim 1982a) together with the merits and limitations of the technique.

3. Results and discussion

The decovoluted first differential ie curves for $C_6H_5^+$ fragment ions produced from toluene, n-propylbenzene and acetophenone studied for 3–4 eV above threshold are given in figures 1–3. The ae threshold and higher energy values are compiled in table 1, together with previously available reported values for ae at threshold only. ΔH_f values for $C_6H_5^+$ ion calculated from our ae values are also introduced in table 1 together with previously reported ΔH_f values for the same ion from different sources. The ae values reported in table 1 are the average of four determinations and the errors quoted are the standard deviations. Only reproducible values are reported in table 1.
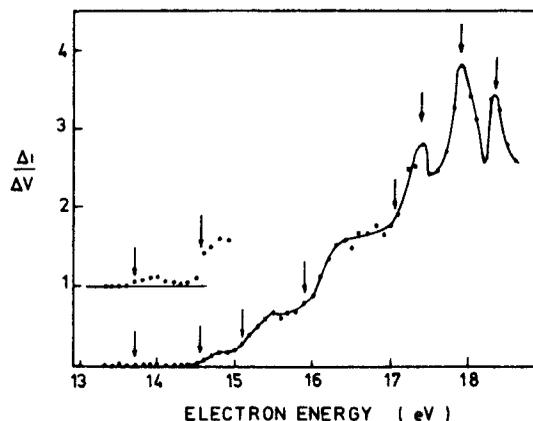
Figure 1.   The deconvoluted first differential ie curve for $C_6H_5^+$ ($m/z = 77$) fragment ion obtained from toluene.
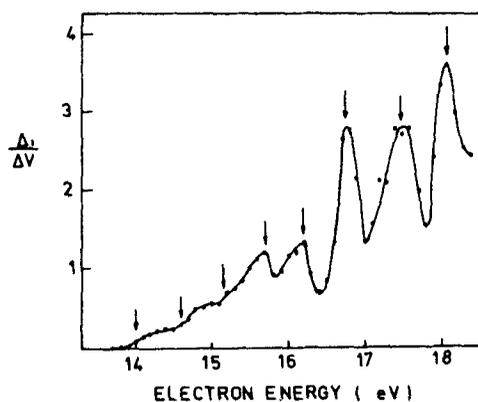
Figure 2. The deconvoluted first differential IE curve for $C_6H_5^+$ ($m/z = 77$) fragment ion obtained from *n*-propylbenzene.
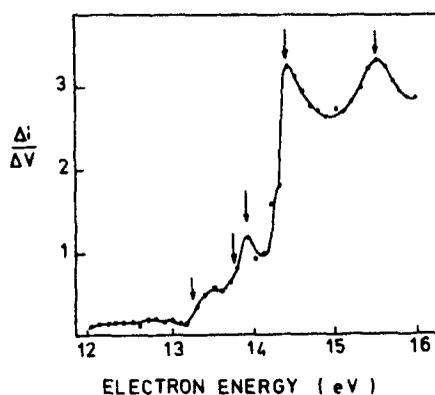

Figure 3. The deconvoluted first differential IE curve for $C_6H_5^+$ ($m/z = 77$) fragment ion obtained from acetophenone.

3.1 $C_6H_5^+$ *fragment ion from toluene*

The IE curve for $C_6H_5^+$ ion ($m/z = 77$) produced from toluene exhibits a relatively long tail (more than 1 eV) at threshold leading to a very low cross-section for the process forming the AE at threshold which is measured at 13·75 eV and is in good agreement with the value (13·70 eV) reported by Majer and Patrick (1962) and Kandel (1954). A wealth of structure have been detected in the deconvoluted first differential IE curve of the ion from toluene but in the absence of theoretical and experimental data one finds it difficult to interpret this structure.

The calculated ΔH_f value for $C_6H_5^+$ ion at threshold is equal to 1238 kJ mol^{-1} and is corresponding to acyclic structure which probably rules out the formation of $C_6H_5^+$ from toluene with phenyl structure. It is worth noting that the results reported by Kandel (1954) and Majer and Patrick (1962) lead to ΔH_f value, for $C_6H_5^+$ ion obtained from toluene, corresponding also to acyclic structure. The formation of

Table 1. AE's and heats of formation for $C_6H_5^+$ fragment ion ($m/z = 77$) obtained from toluene, n-propylbenzene and acetophenone.

Source	AE's (eV)		Heat of formation (kJ mol^{-1})	
	This work	Previous determination	This work	Previous determination
Toluene	13.75 ± 0.12	13.70 ± 0.1[a] 13.70 ± 0.05[b]	1238	1234[a]
	14.56 ± 0.09			
	15.02 ± 0.10			
	16.00 ± 0.11			
	17.21 ± 0.09			
	17.38 ± 0.12			
	17.81 ± 0.12			
	18.25 ± 0.13			
	14.10 ± 0.06		1276	—
	14.59 ± 0.06			
	15.14 ± 0.08			
	15.68 ± 0.07			
n-propylbenzene	16.12 ± 0.09			
	16.80 ± 0.10			
	17.53 ± 0.11			
	18.12 ± 0.09			
Acetophenone	13.21 ± 0.09			
	13.47 ± 0.07	13.50[c], 13.42[d]	1150	1180[c], 1171[d]
	13.62 ± 0.13			
	14.36 ± 0.10	14.23 ± 0.05[e]	1261	1251[e]
	14.50 ± 0.20			

(a) Majer and Patrick 1962; (b) Kandel 1954; (c) Majer and Patrick 1963; (d) Foffani *et al* 1963; (e) Natalis and Franklin 1965.

$C_6H_5^+$ fragment ion from toluene molecular ion by abstraction of CH_3 radical is either by simple cleavage of phenyl-methyl bond or by some sort of rearrangement in the molecular ion before forming $C_6H_5^+$ and CH_3. The ΔH_f value obtained presently for $C_6H_5^+$ at threshold rules out the formation of the ion by simple cleavage. This finding agrees completely with the opinion of Grubb and Meyerson (1963) who reported that the interpretation of the available data in terms of simple cleavage of phenyl-methyl bond proved to be based on erroneous assumptions.

3.2 $C_6H_5^+$ fragment ion from n-propylbenzene

The AE at threshold for $C_6H_5^+$ fragment ion ($m/z = 77$) obtained from n-propylbenzene is measured at 14.10 eV. No available similar value was previously reported in the literature to compare with. Higher AE have been detected in the IE curve of the ion at 14.59, 15.14, 16.12, 17.53 and 18.12 eV and can be correlated, within experimental errors, with similar higher AE values measured in the IE curve of $C_6H_5^+$ ion produced from toluene at 14.56, 15.02, 16.00, 17.38 and 18.25 eV, respectively. The similarity between the structure obtained from the two IE curves is probably an evidence for a common source responsible for the appearance of the structure and is probably pre-ionization in origin.

The calculated ΔH_f value for $C_6H_5^+$ obtained from *n*-propylbenzene at threshold is equal to 1276 kJ mol^{-1} and does correspond to the phenyl structure but to an acyclic (linear) structure for the fragment ion. If one compares the ΔH_f value for $C_6H_5^+$ obtained from *n*-propylbenzene (1276 kJ mol^{-1}) to that obtained from toluene (1238 kJ mol^{-1}) one may suggest that the process of formation of $C_6H_5^+$ from *n*-propylbenzene is associated with about 0·4 eV of excess energy. Similar to the case of toluene one may suggest that the $C_6H_5^+$ fragment ion is obtained from *n*-propylbenzene by some sort of rearrangement of the molecular ion and not by simple cleavage of C_3H_7 radical.

3.3 $C_6H_5^+$ *Fragment Ion from acetophenone*

The deconvoluted first differential IE curve for $C_6H_5^+$ ion produced from aceto-phenone exhibits a relatively long tail at threshold and a very sharp rise at about 14·20 eV. The previously reported AE values for the ion at threshold measured by Majer and Patrick (1963) at 13·50 eV and Foffani *et al* (1963) at 13·42 eV probably do not correspond to the first AE for the ion but to the second one. These AE can be correlated to the presently measured second AE at 13·59 eV. Also the high AE value at threshold for the ion reported by Natalis and Franklin (1965) at 14·23 eV probably corresponds to a higher AE since it can be correlated with our fourth detected AE at 14·36 eV.

The ΔH_f value calculated for the ion at threshold is equal to 1150 kJ mol^{-1}. This value is in good agreement with ΔH_f value reported previously for the phenyl ion (calculated from ionization energy of C_6H_5 radical) by Lossing *et al* (1964) suggesting that $C_6H_5^+$ produced from acetophenone at threshold has a phenyl ion structure. The path of formation of $C_6H_5^+$ fragment ion from acetophenone was established by Grubb and Meyerson (1963) based on the detection of two metastable peaks at masses 91·9 and 56·7. These two metastable peaks confirm the following two reactions which indicate that $C_6H_5^+$ fragment ion is obtained from $C_7H_5O^+$ fragment ion and not from acetophenone molecular ion by elimination of CO:
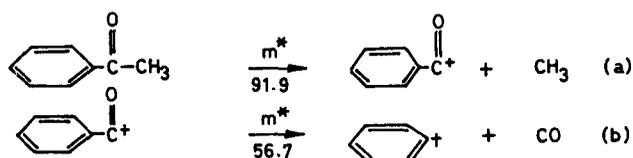
These dissociation paths agree with our results concerning the formation of $C_6H_5^+$ at threshold with phenyl structure since according to reaction (b) CO is eliminated from $C_7H_5O^+$ by simple cleavage to form $C_6H_5^+$ fragment as phenyl ion.

It is possible that at energy higher than the threshold, $C_6H_5^+$ fragment ion can be formed from acetophenone with the less stable acyclic structure. There is supporting evidence for this from the higher AE for this ion. The calculated ΔH_f value corresponding to the fourth AE, for $C_6H_5^+$ fragment ion obtained from acetophenone, at 14·36 eV is equal to 1261 kJ mol^{-1}. The latter value is in agreement with ΔH_f value for the linear ion obtained at 1255 kJ mol^{-1} by Momigny *et al* (1962). The formation of $C_6H_5^+$ as an acyclic ion at the fourth AE indicates that the second and third AE for

$C_6H_5^+$ formed from acetophenone at 13·47 and 13·62 eV (table 1) respectively correspond to two excited states for the phenyl ion formed at threshold.

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